

THE CRYSTAL STRUCTURE OF ANTHRACENE AT DIFFERENT TEMPERATURES*

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Plate XIV

ABSTRACT. The crystal structure of anthracene at -180°C , 32°C , 55°C and 80°C has been investigated by studying the Debye-Scherrer patterns. It is found that at a temperature of about -180°C the dimensions of the unit cell are given by $a = 8.547$ A.U., $b = 6.000$ A.U., $c = 11.090$ A.U. and $\beta = 125^{\circ}10'$. These values a , b and c being slightly lower than those at the room temperature. The mean values of α_a , α_b and α_c , the coefficients of expansion along the three crystallographic axes a , b and c respectively are found to be 77.5×10^{-6} , 27.52×10^{-6} and 31.05×10^{-6} respectively. The dimensions of the unit cell of the crystal at 80°C are $a = 8.696$ A.U., $b = 6.150$ A.U., $c = 11.310$ A.U. and $\beta = 124^{\circ}28'$. It appears that the coefficient of expansion is low upto about 55°C but a tenfold increase in the values takes place in the range from 55°C to 80°C . The values for α_a , α_b and α_c in the range from 32°C to 80°C are 32.55×10^{-5} , 39.36×10^{-5} and 27.45×10^{-5} respectively.

INTRODUCTION

The crystal structure of anthracene was first determined by Bragg (1923) by the X-ray reflection method who observed that the crystal belongs to a space group C_{2h}^5 with the unit cell dimensions, $a = 8.58$ A.U., $b = 6.02$ A.U., $c = 11.18$ A.U. and $\beta = 125^{\circ}$. The space group was confirmed by Banerjee (1930) who studied the Debye-Scherrer patterns and the rotation photographs due to the crystal. The structure was determined more accurately by Robertson (1933) employing the double Fourier series method and by Mathieson, Robertson and Sinclair (1950) by the triple Fourier series method. These authors reported the same space group for the crystal, but slightly different unit cell dimensions. The values given by them are $a = 8.561$ A.U., $b = 6.036$ A.U., $c = 11.163$ A.U. and $\beta = 124^{\circ}42'$.

The mean values of coefficients of expansion α_{11} , α_{22} and α_{33} over the range 20° to -195°C were reported by Kozhin and KitaiGorodskii (1953) to be 111.7×10^{-6} , 13.4×10^{-6} and 20.3×10^{-6} respectively. They reported the unit cell dimensions at 20°C as $a = 8.544$ A.U., $b = 6.023$ A.U., $c = 11.145$ A.U. and $\beta = 124^{\circ}42'$ and at -195°C as $a = 8.441$ A.U., $b = 6.006$ A.U., $c = 11.08$ A.U. and

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$\beta = 125^\circ 35'$. So there is no change in the lattice of crystal in the temperature range from 20°C to -195°C .

It is known now that the lattice of *p*-dichlorobenzene changes when the crystal is heated to about 45°C . It was thought worthwhile to find out whether the structure of anthracene remains unaltered or changes above room temperature. The Debye-Scherrer pattern of the crystal was therefore studied at 55°C and 80°C and also at -180°C in order to compare with each other the structures at these temperatures.

EXPERIMENTAL

Anthracene used was of chemically pure quality supplied by J. T. Baker Chemical Co., U.S.A. The substance was powdered well in a mortar and packed inside a glass tube of diameter 0.7 mm and the Debye-Scherrer pattern was photographed at different temperatures. The methods for keeping the powder at the temperature of liquid oxygen and also at temperatures higher than 32°C were the same as those described by Krishna Murti and Sen (1956).

A Seifert X-ray tube running at 26 ma, 32 kV was used to photograph the patterns. An exposure of about $2\frac{1}{2}$ hrs was sufficient to get the pattern recorded with moderate density. The rings obtained were sharp since the diameter of the sample was about $\frac{1}{2}$ mm. The X-ray tube was provided with a copper target and a nickel filter was used to cut off the $K\beta$ wavelengths. Two cylindrical cameras were used and the radii of the cameras were measured accurately by taking the Debye-Scherrer pattern of rocksalt. For the high temperature camera, the distance from the film to the specimen is 2.84 cms and for the low temperature and room temperature camera, it is 5.25 cms. Several photographs under the same conditions were taken for each specimen to test the genuineness of the results. Spacings were calculated from the diameters of the Debye-Scherrer rings which were measured correct to about 0.1 mm.

RESULTS AND DISCUSSION

The spacings deduced from the Debye-Scherrer patterns due to the crystal at different temperatures mentioned above are given in Table I in which the spacings calculated from the data of Mathieson, Robertson and Sinclair (1950) are also included in the first column for comparison. The intensities of the ring are recorded as very strong (vs), strong (s), medium (m), weak (w) and very weak (vw). Some of the representative photographs of the Debye-Scherrer patterns obtained under different conditions are reproduced in Plate XIV.

It can be seen from Table I that the spacings observed for the crystal at room temperature (32°C) agree fairly well with the spacings calculated from the data given by Mathieson, Robertson and Sinclair (1950). The assignment of indices to the planes was made by taking the structure factors of different planes

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TABLE I
Spacings of crystals of anthracene

Planes	Spacing	Present Investigation				Cooled to 180°C and brought back to 32°C
		at 32°C	at 55°C	at 80°C	at 180°C	
001	9.128	9.120 w			*9.083 vw	9.120 w
101	8.318					
100	7.041					
010	6.036					
102	5.526					
011	5.034					
111	4.885	4.888 w	4.888 vw	*4.977 vw	*4.867 vw	4.888 w
110	4.581	4.577 vs	4.577 vs	*4.666 vs	*4.557 vs	4.577 w
002	4.564					
101	4.478					
201	4.179	4.184 s	4.184 s	*4.244 s	*4.144 s	4.184 s
202	4.159					
112	4.076					
103	3.651					
012	3.641					
111	3.596					
200	3.520	3.525 s	3.525 s	3.584 s	3.490 s	3.525 s
203	3.483					
211	3.436	3.440 s	3.440 s	3.494 s	3.419 s	3.440 s
104	3.349					
102	3.107					
003	3.043					
210	3.040	3.042 s	3.042 s	*3.094 s	*3.018 s	3.042 s
020	3.018					
113	2.868					
021	2.866	2.866 w	2.866 vw	*2.925 vw	*2.848 vw	2.866 w
121	2.836					
201	2.794					
120	2.774	2.777 w	2.777 vw	*2.825 vw	*2.759 vw	2.777 w
204	2.763					
112	2.761					
013	2.717					
301	2.672					
211	2.535					
022	2.517					
121	2.503					
221	2.446					
311	2.443	2.444 m	2.444 m	2.482 m	2.428 w	2.444 m
114	2.433					
103	2.348					
300	2.347					
220	2.291					
004	2.282	2.280 w	2.280 vw	*2.333 vw	2.268 w	2.280 w
202	2.239					
205	2.217					
113	2.189					
310	2.187					
122	2.165					
014	2.134					
212	2.092					
105	2.078					

TABLE I (Contd.)

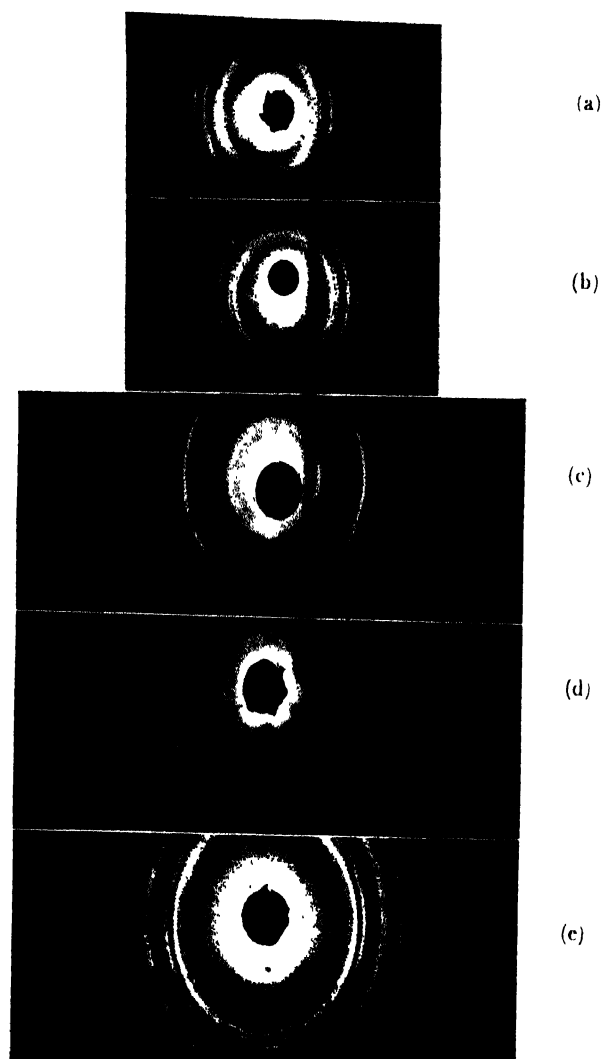
From the data of Mathieson, Robertson & Sinclair (1950)		Present Investigation				Cooled to -180°C and -brought back to 32°C
Planes	Spacings	at 32°C	at 55°C	at 80°C	at -180°C	
221	2.050	2.052 mw	2.052 mw	2.080 vw	2.035 w	
224	2.038			(broad)		
301	2.015					
030	2.012					
321	2.001	2.004 vw			1.987 vw	2.004 vw
031	1.964	1.968 vw				1.968 vw
131	1.956					
130	1.934	1.930 vw			1.922 vw	1.930 vw
311	1.912					
104	1.879					
411	1.853	1.855 m	1.855 m	1.884 m	1.840 m	1.855 m
320	1.852					
203	1.841					
131	1.835					

* These spacings are used to calculate dimensions of the unit cell.

TABLE II

Planes	Spacings in A.U. at -180°C		Spacings in A.U. at 80°C	
	Calculated from unit cell dimensions	observed	Calculated from unit cell dimensions	observed
200	3.493	3.493	3.584	3.584
211	3.420	3.419	3.494	3.494
311	2.428	2.428	2.482	2.482
004	2.267	2.268		
221	2.035	2.035	2.090	
321	1.988	1.987	2.070	2.080 (broad)
130	1.922	1.921		
411	1.841	1.840	1.885	1.884

into consideration. It can be seen from Table I that the spacings at 32°C agree with those given by Mathieson, Robertson and Sinclair (1950) and therefore the dimensions of unit cell are given as $a = 8.561$ A.U., $b = 6.036$ A.U., $c = 11.163$ A.U. and $\beta = 124^\circ 42'$ as reported by those authors.



Debye-Scherrer pattern of anthracene

- (a) Specimen at 80°C (Radius of Camera : 2.84 cms)
- (b) Specimen at 55°C (Radius of Camera : 2.84 cms)
- (c) Specimen at 32°C (Radius of Camera : 5.25 cms)
- (d) Specimen at -180°C (Radius of Camera : 5.25 cms)
- (e) Specimen once cooled to -180°C and brought back to 32°C (Radius of Camera : 5.25 cms).

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It is further evident from the Table I that all the spacings for the crystal maintained at -180°C are consistently shorter than the corresponding spacings for the crystal at 32°C and when the crystal is brought back to 32°C , after it is once cooled to -180°C , the spacings agree with those at room temperature. Since new Debye-Scherrer rings do not appear in the pattern obtained for the crystal at -180°C , it can be concluded that the unit cell only contracts at -180°C and no appreciable distortion takes place. The dimensions of the unit cell calculated from the spacings of the planes (001), (111), (110), (120), (210) and (021) for the crystal at -180°C are given below.

$$\begin{aligned}a &= 8.547 \text{ A.U.} & b &= 6.000 \text{ A.U.} \\c &= 11.090 \text{ A.U. and} & \beta &= 125^{\circ}10' .\end{aligned}$$

Taking the dimensions of the unit cell for the crystal at room temperature as those reported by Mathieson *et al* (1950) the mean coefficients of expansions, α_a , α_b and α_c in the directions along the three crystallographic axes in the range 32°C to -180°C can be calculated. The calculated values are

$$= 77.5 \times 10^{-6}, \quad \alpha_b = 27.52 \times 10^{-6} \quad \alpha_c = 31.05 \times 10^{-6}.$$

The dimensions of the unit cell for the crystal at -195°C reported by Kozhin and KitaiGordskii (1953) agree fairly well with those obtained in the present investigation excepting the value of a . But since they reported values for the dimensions of the unit cell at 20°C lower than those reported by Mathieson *et al* (1950) the mean values of coefficients of expansion do not agree with those obtained from the data reported by them.

It can be seen from Table I that the spacings for the crystal at 80°C are comparatively higher than those obtained for the crystal at 32°C . But as no new rings appear in the Debye-Scherrer pattern nor does the pattern change even slightly when the crystal is heated to 80°C , it can be concluded that only thermal expansion of the unit cell takes place with the rise of temperature to 80°C . The dimensions of the unit cell in the crystal at 80°C calculated from spacings of (11 $\bar{1}$), (110), (120), (004), (021) and (20 $\bar{1}$) are found to be

$$\begin{aligned}a &= 8.696 \text{ A.U.} & b &= 6.150 \text{ A.U.} \\c &= 11.310 \text{ A.U. and} & \beta &= 124^{\circ}28' .\end{aligned}$$

The mean values of coefficients of expansion α_a , α_b and α_c in the range from 32°C to 80°C are obtained as

$$\alpha_a = 32.85 \times 10^{-5}, \quad \alpha_b = 39.36 \times 10^{-5} \quad \text{and} \quad \alpha_c = 27.45 \times 10^{-5}.$$

It can be seen that the mean values of coefficients of expansion in the high temperature range are about ten times higher than those in the low temperature region.

It can be seen from Table I that the values of spacings in the crystal at 55°C are almost the same as those for the crystal at 32°C. This might be due to the reason that in this temperature range the coefficient of expansion is small so that appreciable change in the spacings does not take place. The spacings, however, increase abruptly when the temperature is raised above 55°C and the coefficient of expansion increases enormously. The values of the spacings of other planes calculated from the dimensions of the unit cell for the crystal at low and high temperatures are given in Table II together with those observed. It can be seen that these two sets of values agree fairly well with each other.

The low frequency Raman lines of anthracene at different temperatures have not been investigated thoroughly and it would be interesting to find out whether these lines undergo abrupt changes with the change in the temperature of the crystal from 32°C to 80°C, because in the case of *p*-dichlorobenzene such a change has been observed by previous authors.

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